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MINISTRY OF AGRICULTURE, FISHERIES AND FOOD

Fumigation with the Liquid Fumigants
Carbon Tetrachloride, Ethylene Dichloride
and Ethylene Dibromide

PRECAUTIONARY MEASURES
1962



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INTRODUCTION

(1) Various substances are used for the fumigation of commodities against insect pests. The term "liquid fumigant" is used as a convenient way of describing a group of these whose boiling point is sufficiently high for them to be liquid at atmospheric temperatures as distinct from fumigants such as methyl bromide which are gaseous under these conditions and have to be stored in steel cylinders. There are several substances which could be included but this leaflet deals only with those in regular use in the United Kingdom, namely, carbon tetrachloride and ethylene dichloride, and with ethylene dibromide which is sometimes used in association with the other two.

By reason of their lower volatility these liquid fumigants are less hazardous to handle than the gaseous fumigants. They are, nevertheless, highly toxic and great care is necessary if they are to be used safely.

In circumstances where they apply the provisions of the Factories Act 1961, must be observed

PROPERTIES OF THE LIQUIDS

Carbon Tetrachloride

(2) Carbon tetrachloride is a heavy colourless liquid which boils at 76.8°C and has a characteristic odour. It is widely used as a fire extinguisher and as a degreasing solvent in industry and the dry cleaning trade.

(3) In large doses it is both a narcotic and metabolic poison and exposure to high concentrations rapidly causes collapse and loss of consciousness. Symptoms of exposure to concentrations insufficient to cause anaesthesia include severe headaches, nausea, conjunctivitis and prolonged vomiting. Deaths have been recorded, some of which took place rapidly after exposure but most during the period 2-12 days afterwards with symptoms of involvement of the liver or kidneys or both. In less severe cases regeneration of the tissues takes place fairly rapidly and permanent damage from repeated sub-lethal dosage is rare. Habitual alcohol drinkers may be more seriously affected.

The maximum permissible concentration for prolonged exposure is 25 p.p.m. (0.17 mg/l) see footnote on p. 2.

(4) Because of its solvent action on the protective fats of the skin, carbon tetrachloride causes chapping and may predispose to secondary infections.

(5) As a fumigant carbon tetrachloride is not especially toxic to insects and large dosages and long periods of exposure are necessary for successful results. It is rarely used alone except for the treatment of grain in deep silo bins for which its penetrating powers make it particularly useful. In mixtures with other fumigants its fire inhibiting properties as well as its penetrating properties are valuable.

Ethylene Dichloride

(6) Ethylene dichloride, more correctly known as 1,2 dichloroethane or symmetrical dichloroethane, is a colourless liquid of boiling point 83.5°C with a sweet smell resembling that of chloroform. It is used in industry as a solvent.

(7) Ethylene dichloride is a powerful narcotic and poisoning symptoms include dizziness, headache, nausea and vomiting.

The maximum permissible concentration for prolonged exposure is 100 p.p.m. (0.44 mg/l) see footnote.

(8) The solvent action of the substance on the skin has been known to cause severe dermatitis.

(9) Ethylene dichloride is much more toxic to insects than is carbon tetrachloride but by reason of its inflammability it is commonly used in admixture with carbon tetrachloride. Two mixtures are in common use. One contains three parts by volume of ethylene dichloride to one part of carbon tetrachloride, this proportion of the last named being the minimum necessary to give a non-inflammable mixture. The other contains equal parts by volume of the two constituents. The 3:1 mixture is used for fumigating bagged goods and for grain in bulk less than about six feet deep. For grain deeper than this the 1:1 mixture is usually preferred.

Ethylene Dibromide

(10) Ethylene dibromide or 1,2 dibromoethane is a substance of high density (over twice as heavy as water) and of high boiling point (131.6°C). It is normally a colourless liquid but having a freezing point of 10°C (50°F) it may solidify during cold weather. It is non-inflammable.

(11) Experimental work on animals has shown that, in single exposures, ethylene dibromide vapours are slightly more toxic than those of methyl bromide and appreciably more toxic than those of carbon tetrachloride and ethylene dichloride.

The maximum permissible concentration for prolonged exposure is 25 p.p.m. (0.21 mg/l) see footnote.

(12) Ethylene dibromide causes blistering if the liquid is allowed to remain in contact with the skin.

(13) The high toxicity of ethylene dibromide to insects (comparable with that of methyl bromide) and its relatively low volatility make it a valuable constituent of mixtures for treating individual machines without specially sealing them. This technique is usually known as spot fumigation.

Ethylene dibromide has also been used in mixtures for fumigating bulk grain and contributes greatly to the effectiveness of the treatment at the surface but prolonged airing is necessary after fumigation to rid the material of the fumigant.

Footnote: These figures, which relate to average concentrations for a normal working day, are taken from the Ministry of Labour's Safety Health and Welfare Booklet (new series No. 8) entitled "Toxic Substances in Factory Atmospheres", (H.M.S.O. 1960, price 1s., 1s. 3d. by post).

DETECTION

(14) Although the first and obvious method of detecting concentrations of the liquid fumigants dealt with in this pamphlet is by smell, the sense of smell varies greatly from person to person, and may also be affected by colds and catarrh. Furthermore it quickly becomes dulled in the continuous presence of small concentrations. For these reasons, whereas a strong smell is an indication of a dangerous concentration, absence of smell cannot be taken as a certain guide that no gas is present.

(15) Accurate measurement of concentrations of these compounds singly or in admixture is possible but the methods are elaborate and time-consuming and can normally be carried out only in well-equipped laboratories.

Halide detector lamps, which are widely used in connection with fumigation with methyl bromide, also give a response with each of these compounds. These devices are blow lamps of various types modified so that the flame gives a green or bright blue colour in the presence of the compound. The response is variable, however, so that it is not very reliable as a quantitative measure of concentrations around the maximum permissible level. Nevertheless, these lamps are helpful in seeking out pockets of gas; their method of use is described in "Methods for the Detection of Toxic Substances in Air", Booklet No. 12, "Organic Halogen Compounds", H.M.S.O., 1961. Price 1s. 3d. (1s. 6d. by post).

For the measurement of concentrations of ethylene dichloride and of carbon tetrachloride in the region of their maximum permissible concentrations small portable devices of greater reliability than the halide detector lamps are available. These draw a sample of air through a tube containing chemically impregnated silica gel which develops a length of stain or colour change as a measure of the concentration. Using separate tubes each of these compounds can be measured in the presence of the other. At present no suitable detector tubes are available for measurement of ethylene dibromide in the region of the maximum permissible concentration.

Advice on methods for detecting these substances can be obtained on application to the Director, Pest Infestation Laboratory, London Road, Slough, Bucks.

PROTECTIVE EQUIPMENT

Respirators

(16) In all but the smallest treatments it is necessary to use a suitable gas respirator. (*Dust* respirators give no protection against gases). The simplest type is the canister respirator, in which the noxious constituent of the atmosphere is removed by a suitable sorbent before the air is breathed. For the liquid fumigants the appropriate canister is one designed to give protection against "organic vapours". The canister specially designed for methyl bromide could also be used. Canister respirators give protection in atmospheres containing up to 1 per cent of the noxious vapour for a short period but *they are not designed for use in high concentrations or for prolonged periods. They must never be used in confined spaces, where high concentrations are quickly built up.*

For these circumstances either distance breathing apparatus or self-contained breathing apparatus is essential.

Distance breathing apparatus has the advantage that it can be used indefinitely and if pure air is near at hand the apparatus is simple—an air hose attached to the face-piece. If it is necessary to go further than about 60 ft. to ensure the purity of the air however more elaborate means such as bellows or a compressor are required to keep up the supply of air to the user. Whether short or long the hosing is sometimes an encumbrance to the user. Self-contained breathing apparatus avoids this at the expense of greater weight and the disadvantage that the supply is limited. Various types of approved self-contained apparatus are available of which those using compressed air have certain advantages for fumigation work.

Breathing apparatus (including canister respirators) approved by H.M. Chief Inspector of Factories for the purposes of the Chemical Works Regulations, 1922 is listed in Form 893 published by the Factory Inspectorate, Ministry of Labour.

Respirators of all types must be carefully looked after. They should always be checked over before use and cleaned after use.

Protective clothing

(17) No special protective clothing is necessary when using ethylene dichloride and carbon tetrachloride but for handling ethylene dibromide or mixtures containing it protective gloves should be worn. They must be carefully looked after and protected from damage. The presence of cuts or pinholes through which vapour could pass, subsequently to be kept in contact with the skin, would render the use of the gloves more hazardous than working without them. Gloves which are damaged or suspect should be discarded.

PRECAUTIONS WHEN USING ETHYLENE DICHLORIDE AND CARBON TETRACHLORIDE

(18) As the hazards of using the liquid fumigants vary greatly with the circumstances it will be necessary to consider the main classes of fumigation and to deal with the safety precautions separately for each. In all cases careful planning of the operation with these precautions in mind will greatly reduce the risks.

The Fumigation of Grain in Deep Silo Bins

(19) A common method of fumigating grain in deep silo bins i.e. bins of fifty foot depth or more with closed tops such as are to be found in the main ports is to apply carbon tetrachloride to the grain surface and to leave the bin shut for not less than a week.

(20) After the carbon tetrachloride has been applied a separate application of ethylene dichloride is occasionally made to ensure adequate treatment of the grain surface. This addition does not call for any precautions beyond those outlined below.

On the other hand the addition of methyl bromide to the carbon tetrachloride to produce a more toxic fumigant does increase the hazards and this mixture should only be used by those experienced in the use of methyl bromide and familiar with the safety precautions detailed in the Home Office Advisory Pamphlet "Fumigation with Methyl Bromide: precautionary measures" (H.M.S.O. 1960, price 6d.).

Precautions before treatment is commenced

(21) The slides at the bottom of the bins being treated must be sealed to prevent leakage of fumigant. To guard against premature discharge of the grain they should be clearly labelled and if possible locked in position.

As much ventilation as possible should be given to working spaces at bin top and bin bottom level.

Staff not directly engaged should be excluded from the vicinity of the treatment.

Precautions when applying the fumigant

(22) At least two operators should be employed, one being designated as in charge. All should have had instruction in the properties of the liquid fumigants and in the precautions necessary and the operator in charge should have had previous experience in fumigating with them.

The operators must remain outside the bin using a suitable self-priming pump to spray the liquid evenly over the surface of the grain, care being taken to avoid leakage of liquid from the pump or its hose connections. They must wear suitable breathing apparatus. A canister respirator of approved pattern will normally be adequate but for prolonged operations in poorly ventilated buildings distance breathing apparatus or self contained breathing apparatus may be required (see para. 16).

At the conclusion of the application the bin top cover should be sealed and a danger label affixed.

Precautions during the exposure period

(23) As much ventilation as possible should be given to spaces at bin bottom level. Penetration of carbon tetrachloride to the bottom of a deep bin may take many hours consequently there is little likelihood of leakage from the bottom of the bin until some time after the application of the fumigant and this may lead to a false sense of security. Working spaces at bin bottom level should be kept under inspection particularly if the ventilation is poor and no one should be allowed to remain there if gas can be detected (see paras. 14 and 15). Similarly no one should be allowed to enter bins adjacent to those treated until they have been ventilated and found free of gas.

Precautions when the grain is moved

(24) Care must be taken to see that workmen are not exposed to harmful concentrations in band tunnels or other spaces through which the grain moves. The empty bin should be left open top and bottom for at least twenty-four hours before anyone is permitted to enter it. If the grain is turned to another bin no one should be permitted to enter the space above the grain in the new bin until it is clear of gas.

The Fumigation of Grain in Small Bins or in Bulk on the Floor

(25) In this class of treatment the depth of grain rarely exceeds twenty feet and mixtures of ethylene dichloride and carbon tetrachloride are normally used.

The essential safety precautions comprise: exclusion of people other than the fumigators from the fumigation area and its immediate vicinity for as long as harmful concentrations of gas are present; protection of the fumigators

themselves from contact with the liquid and from breathing the gas; and provision for adequate airing of the foodstuffs before consumption.

The detailed arrangements necessary vary with the size of the fumigation.

Protection of workpeople

(26) All those not engaged in the application of the fumigant should be excluded from the fumigation area and from all adjacent spaces into which gas might penetrate. Animals should also be excluded from these areas. Where possible the rooms or buildings concerned should be locked and the fumigator in charge should take possession of the keys. The keys should not be released until the spaces are clear of gas.

Where the quantity of fumigant used is small, say less than ten gallons, people and animals need only be kept away from the vicinity of the fumigation for a short while. In large scale treatments however it will often be necessary to exclude them for the whole of the exposure period and until the fumigant has been aired off afterwards. Particular care is needed in farm buildings in which animals are kept in a room separated only by a partition from a space containing grain under fumigation.

Protection of the fumigators

(27) At any fumigation however small at least two workers should be present. *For very small treatments*, where each man will not be applying more than five gallons of liquid and the work is being done in a well ventilated space it may be possible to dispense with the use of respirators but in all other cases respirators of suitable type must be worn (see para. 16). For work involving large quantities of fumigant and for work in confined spaces distance breathing apparatus or self contained breathing apparatus is necessary. Such apparatus must be worn for work in a partly filled bin even if this has an open top.

If it is necessary to walk on freshly sprayed grain e.g. to cover the surface, rubber boots should be worn.

Removal of residual fumigant

(28) During the fumigation period some of the fumigant is taken up by the commodity. There is no chemical combination as there is with some other fumigants but the removal of the residual fumigant is a slow process and cases are on record of animals becoming ill through being given food which had not been aired sufficiently after fumigation.

For grain in shallow bulks on the floor a week's airing should be allowed if it is to be fed whole to animals. A shorter time would be sufficient if the grain were spread out in a thin layer or if it were milled before use.

In bins or in deep bulks the airing of the grain beneath the surface will be particularly slow and before using grain from the bottom of such bulks it should be exposed for a day or two in bags or in a thin layer on the floor.

The Fumigation of Bagged Commodities and Empty Sacks

(29) Small quantities of bagged cereals, cereal products and other goods and also bundles of empty sacks can be fumigated effectively with the 3:1 mixture of ethylene dichloride and carbon tetrachloride. The process usually consists in placing the goods in a suitable container (for example a metal bin or a wrapping of gas proof sheeting), sprinkling them with the liquid and

closing the container. The dosage given varies with the commodity, finely divided materials receiving more than grains, but it is always higher than is used for grain in bulk because a shorter period of exposure is usually allowed (48 or 72 hours compared with 7 days or more). The process is not well suited to the fumigation of large stacks, for which fumigation with one of the gaseous fumigants such as methyl bromide is usually much more effective.

(30) The safety precautions necessary are similar to those described in the previous section and may be summarised as:

- (i) A second person should be present in case of accident even if the work is sufficiently small to be done easily by one person;
- (ii) all other persons or animals should be excluded from the vicinity both at the time of the treatment and subsequently until the space is clear of gas;
- (iii) the fumigators should avoid breathing the vapour. If the work has to be done in a poorly ventilated place or if more than 5 gallons of liquid is used respirators should be worn;
- (iv) the fumigators should keep the liquid off the skin and clothing. Accidental splashes should be washed off immediately and splashed clothing removed;
- (v) when the space is opened up at the end of the exposure period care should be taken to protect persons and animals during the preliminary dispersal of the fumigant;
- (vi) several days' airing must be allowed before fumigated materials are used for food. A few hours airing is usually sufficient to remove all smell of fumigant from empty sacks.

ADDITIONAL PRECAUTIONS WHEN USING MIXTURES CONTAINING ETHYLENE DIBROMIDE

(31) For the fumigation of grain in bulk, liquid fumigant mixtures containing up to 5 per cent of ethylene dibromide by volume have occasionally been used. Mixtures containing up to 20 per cent of ethylene dibromide have been used for the treatment of milling machinery and conveyors by the spot fumigation technique. The use of ethylene dibromide in these mixtures brings additional hazards. Not only is its acute toxicity greater than that of ethylene dichloride and carbon tetrachloride but the liquid blisters the skin and the vapour irritates the eyes. Furthermore a much longer time is needed for removal of the residual fumigant from the commodity after fumigation. The additional safety precautions needed when using it are outlined below.

Making up the mixtures

(32) It is best to purchase fumigant mixtures containing the requisite proportion of ethylene dibromide already mixed by the suppliers but if the mixing has to be done at the time of use a respirator of approved pattern must be worn and gloves impervious to ethylene dibromide must be worn.

Fumigating grain

(33) The precautions listed in paragraph 25-27 apply but the work should be done only by experienced fumigators and a longer period of airing must be

allowed before the grain is used for food. If the grain is processed before consumption e.g. milled and/or cooked not less than three weeks airing is necessary. In the absence of processing a much longer period must be allowed depending on the depth of the grain and on the amount of ventilation which can be given.

The use of ethylene dibromide in fumigant mixtures for use on the farm is not normally recommended.

Using the spot fumigation technique

(34) The work must be done by at least two men, working together, one being designated as in charge. The one in charge should have received special instruction in the safe use of the fumigant.

Protective gloves and an effective respirator must be worn and the equipment used for applying the liquid must be well maintained and free from leaks.

The work must not be commenced until the machinery has been shut down and the staff not engaged in the fumigation have left the vicinity. They must not be readmitted until the space is clear of gas.

FIRST AID MEASURES

(35) The person affected must be removed at once into fresh air, where, after contaminated clothing has been discarded he should be kept warm and allowed to rest. Medical attention should be obtained and, if breathing has stopped or shows signs of failing, artificial respiration must be applied immediately.

Contaminated clothing must be removed and aired well before reuse. Where the skin has been splashed it should be washed with soap and water. If the eyes are affected they should be irrigated thoroughly with water.

In cases of slight over-exposure to the vapour, symptoms, which include headache, nausea and intermittent vomiting, may not appear for an hour or two. If they do appear the patient must rest and obtain medical advice.



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Printed in England by The North Western Printers Ltd., Stockport

and published by

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